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Electrolytic deposition of copper–aluminium alloys and certain of their properties

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The process of electrolytic deposition of copper–aluminium alloys from a nonaqueous ethylbenzene–toluene bath was studied using an electrical system consisting of two independent current circuits to control cathode alloy deposition and anode copper dissolution separately. The influence of electrical parameters on current efficiency and chemical composition of the Cu–Al alloys was determined, as was the phase composition, microhardness and surface morphology. In alloys containing about 10% Al the presence of a martensitic β_1' phase was detected. Due to the very fine-grained structure of the electrolytic alloys obtained, no shape memory effect was observed in copper microelements with Cu–10.6%Al alloy coatings.

1. Introduction

The copper–aluminium alloys possess a number of important physical and mechanical properties making them the preferred choice, rather than the pure metals, for application in many branches of engineering. Aluminium bronzes offer not only useful strength properties and considerable corrosion resistance but also the possibility of thermoelastic martensitic transformations, with which are associated the 'shape memory' effect that has recently been the subject of intensive study [1]. In these circumstances it is of obvious practical advantage to try and master the process of electrolytic deposition of Cu–Al alloy coatings. It is known that the electrolytic deposition of aluminium from aqueous solutions is not possible and hence for this purpose a number of nonaqueous solutions are used, of which xylene [2], ethylbenzene [3] and toluene [4] have proved sucessful as solvents. The salt most commonly used in the bath is aluminium bromide. Exhaustive tests on the electrodeposition of aluminium from alkylbenzene electrolytes were carried out by Capuano and Davenport [5, 6]. These authors used an anode containing about 5% copper in the deposition process and obtained at the cathode a Cu–Al alloy containing up to 3.5% copper [7].

Investigations reported here were undertaken to study certain aspects of the electrolytic process for obtaining Cu–Al alloys from an ethylbenzene–toluene bath. The characteristics of certain Cu–Al alloy coatings were established, providing new data on this subject.

2. Experimental methods

In these tests on the electrodeposition of Cu–Al alloy, the initial galvanizing bath was filled with a 50% solution of aluminium bromide in an equal volume mixture of ethylbenzene and toluene. The aluminium bromide was obtained from the reaction of dry, liquid bromine with metallic aluminium. The bromine was dropped on to aluminium chips placed in a distillation retort whose lateral tube was shut off with a container filled with anhydrous calcium chloride. The retort was heated, first to initiate the reaction and then in order to maintain the aluminium bromide formed in a liquid state.

The quantity of aluminium was calculated so that some remained after reacting the whole volume of bromine. After cooling, a measured portion of the ethylbenzene–toluene mixture was poured on to the reacted mixture and the aluminium bromide that had been formed was removed from the walls by shaking. After filtering, a dark brown liquid was obtained which smoked strongly

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in air: this was used in the deposition tests. The volume of bromine, ethylbenzene and toluene used was chosen such that the concentration of aluminium bromide in the bath was about 50% by weight. The density of the freshly prepared bath was 1.54 kg m^{-3} and its specific conductance was 3.9×10^{-3} Ω^{-1} cm^{-1}.

The alloy coatings were deposited on polycrystalline silver cathodes cut in the form of discs of diameter 1.5×10^{-2} m. The deposition process was carried out in an electrolytic vessel with two chambers separated by a sintered glass partition (Fig. 1). Two electric circuits were used, fed independently from two stabilized d.c. sources. In the main circuit the deposition of the Cu–Al alloy layer on the silver cathode and dissolution of the aluminium anode took place. In the ancillary circuit the current flowed between a dissolving copper anode and a platinum cathode with considerably larger working surface than the anode. The platinum cathode potential was so low that no deposition of metal took place on it. The purpose of the ancillary circuit was to supply copper ions to the bath. The deposition process was carried out at a temperature of 298 K, maintaining an argon atmosphere to protect the bath against the effects of moisture and oxygen from the air. Prior to coating, the silver cathode was polished mechanically and then chemically in a chromium solution [8], after which it was pickled in nitric acid and rinsed in water, methyl alcohol and ethylbenzene.

The current efficiency of the deposition process was determined by weighing. Deposition time was chosen so that the coating thickness was about 1×10^{-5} m. Atomic absorption was employed to determine the chemical composition of the alloys and the plating bath, using a Perkin-Elmer M-603 spectrophotometer. The deposited alloy was completely dissolved in concentrated hydrochloric acid with the addition of a few drops of 20% nitric acid. The solution was next diluted with water to a volume of 100 cm^3 and the content of aluminium and copper was determined. To determine the concentration of aluminium and copper in the bath, 1 cm^3 of the solution was taken and diluted with a few cubic centimetres of methyl alcohol and then heated to boiling point with an equal volume of concentrated sulphuric acid. This solution was then diluted with water to a determined volume and analysis was performed by atomic absorption spectroscopy.

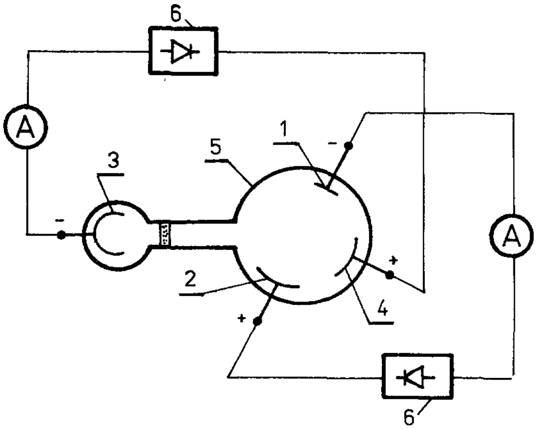

Fig. 1. Diagram of four-electrode cell and circuit used for electrolytic deposition of Cu–Al alloys. 1, silver cathode; 2, aluminium anode; 3, platinum cathode; 4, copper anode; 5, glass vessel; 6, stabilized feed source.

The phase composition of the Cu–Al alloys was determined using a Philips X-ray diffractometer with a graphite monochromator and CoKα radiation. The microhardness of the Cu–Al alloys was measured with a PTM-3 microhardness meter using a 0.294N loading. Surface morphology of the coatings was observed using a Zeiss Neophot-2 metallographic microscope with a magnification of 1000 ×.

3. Results

3.1. *Electrolytic deposition of Cu–Al alloys*

During the process of electrodeposition using a four-electrode system in an ethylbenzene–toluene bath containing from 56 to 57 g dm^{-3} of Al, it was found that deposits of Cu–Al alloy were formed at the silver cathode, the form and properties of these deposits depending on the chemical composition of the alloy. The chemical composition of the deposited alloy depended primarily on the value of charge Q_{Cu} which flowed in the ancillary circuit and on the anode current density j_{A}^{Cu} (Fig. 2). This relation is complex and is governed by a whole series of factors affecting the current efficiency of the anode copper dissolution and cathode alloy deposition and also on the surface passivation, solvation and complexing of metal ions in the solution.

During deposition the concentration of copper ions in the bath remains at a considerably lower

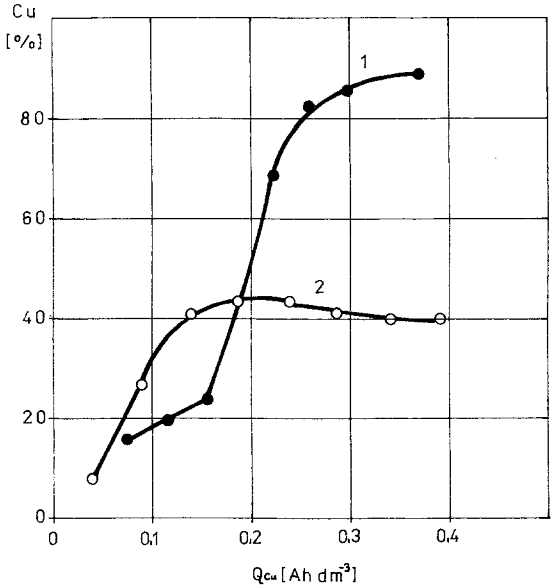

Fig. 2. Percentage content of copper in Cu–Al alloys plotted against values of charge Q_{Cu} flowing in the ancillary current circuit. Bath: ethylbenzene–toluene; anode current density dissolving the copper: 1, $j_A^{Cu} = 1$ A dm^{-2}; 2, $j_A^{Cu} = 2$ A dm^{-2}.

level than the aluminium concentration (Table 1). When using an anode current density of $j_A^{Cu} =$ 2 A dm^{-2}, a virtually constant value of copper concentration in the solution of about 0.15 g dm^{-3} is found, resulting in stabilization of the copper content in the alloy. This may be associated with retardation of the process of anode copper dissolution due to surface passivation. For a lower anode current density of $j_A^{Cu} = 1$ A dm^{-2}, dissolution of the copper is more effective, and at this current density it is possible to obtain Cu–Al alloys with a high copper content. It is surprising that such a relatively small change in copper concentration in the bath causes such a marked percentage rise in copper content in the alloy. Another fact that is difficult to explain is that at the same value of copper content in the bath (about 0.12 g dm^{-3}), when using an anode current density of 2 A dm^{-2} in the ancillary circuit, Cu–Al alloys are obtained having only half the copper content of the alloy obtained using a current density of 1 A dm^{-2} in the copper dissolution circuit. These unexplained facts indicate the complexity of the mechanism of co-deposition of copper and aluminium from the bath in the conditions described.

Table 1. Variations in copper concentration in the bath with increase in charge Q_{Cu} flowing in the ancillary current circuit

$j^A_{Cu} = 1$ A dm^{-2}		$j^A_{Cu} = 2$ A dm^{-2}	
Q_{Cu} (A h dm^{-3})	C_{Cu} (g dm^{-3})	Q_{Cu} (A h dm^{-3})	C_{Cu} (g dm^{-3})
–	–	0.04	0.03
0.08	0.09	0.09	0.08
0.11	0.12	0.14	0.12
0.15	0.16	0.19	0.14
0.23	0.27	0.24	0.15
0.27	0.32	0.29	0.16
0.31	0.34	0.34	0.15
0.38	0.37	0.39	0.14

The current efficiency of the alloy deposition process drops with increasing charge (ΣQ) through the bath (Fig. 3). The value ΣQ, which is the sum of the charges flowing in the main and ancillary current circuits taken relative to the unit volume of the bath, may be taken as the degree of bath exhaustion. With increase in ΣQ, the reduction in current efficiency of the cathode process is greater for a bath richer in copper, from which Cu–Al alloys containing 80 to 90%Cu are deposited.

The fall in current efficiency of the alloy deposition process represents a very serious limitation for the practical utilization of this bath. Studies of the effect of cathode current density on the current efficiency of the process and the chemical composition of the alloy were carried out using a fresh portion of electrolyte for each measurement. Deposition was continued to an equal degree of exhaustion of the bath of $\Sigma Q = 0.3$ A h dm^{-3}, passing a charge of $Q_{Cu} = 0.23$ A h dm^{-3} in the ancillary circuit and using an anode current density of $j_A^{Cu} = 2$ A dm^{-2}.

With increase in cathode current density the percentage content of copper in the alloy and the current efficiency of the process are reduced (Fig. 4). In the range of test current densities used, i.e. from 1 to 3 A dm^{-2}, this reduction has a value of about 13% by weight (copper content) and about 10% in current efficiency. The use of higher current densities causes marked deterioration in the quality of cathode coatings obtained.

3.2. *Characteristics of Cu–Al alloy coatings*

X-ray phase composition analysis was used for Cu–Al alloys containing more than 80% and less

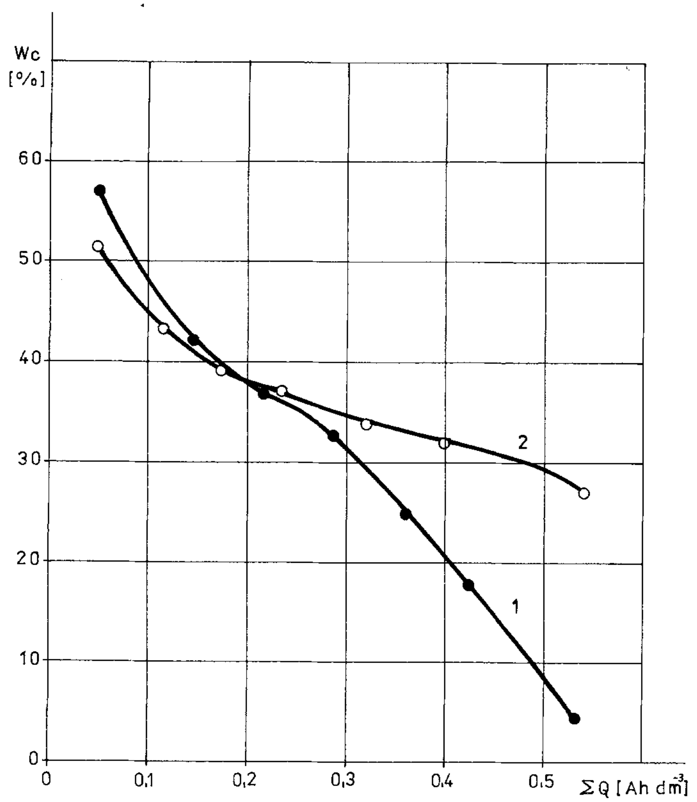

Fig. 3. Current efficiency W_c for cathode deposition of Cu–Al alloy plotted against degree of exhaustion of the ethylbenzene–toluene bath. Anode current density dissolving the copper: 1, $j_A^{Cu} = 1\ \mathrm{A\,dm^{-2}}$; 2, $j_A^{Cu} = 2\ \mathrm{A\,dm^{-2}}$.

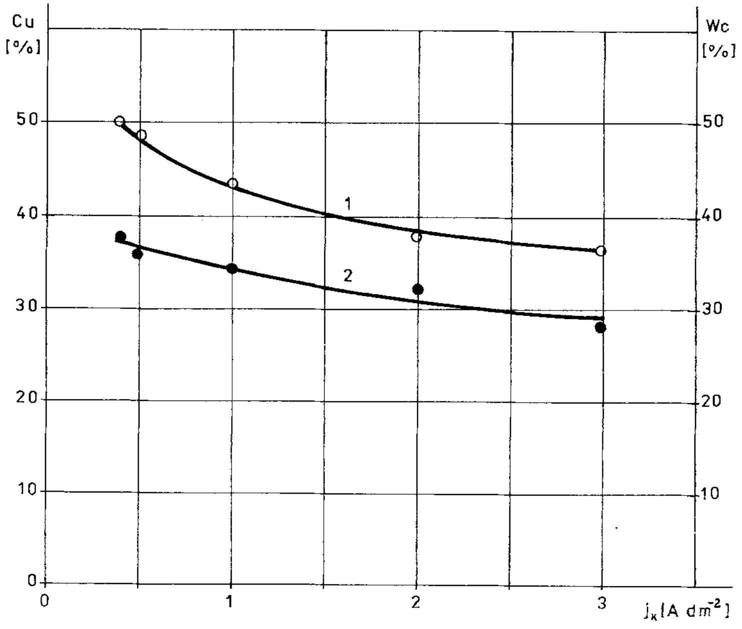

Fig. 4. Percentage content of copper in the Cu–Al alloys (1), and current efficiency W_c in the cathode process of alloy deposition (2), plotted against cathode current density (j_K).

Table 2. Phase composition of Cu–Al alloys

Al in alloy (wt%)	θ	d_{exp}[Å]	d_t[Å]	I/I_0	*Phase*
0.8	25.40	2.087	2.088	100	α-Cu
	29.65	1.809	1.808	46	
	44.45	1.278	1.278	20	
	55.20	1.090	1.093	17	
6.2	25.34	2.091	2.088	100	
	29.49	1.821	1.808	46	
	44.20	1.285	1.278	20	
	54.93	1.094	1.093	17	
8.1	23.55	2.240	2.237	32	β_1'
	25.07	2.112	2.088	100	α-Cu
	26.70	1.994	1.945	90	β_1'
	29.25	1.832	1.808	46	α-Cu
	43.07	1.296	1.278	20	α-Cu
10.3	15.82	3.283	3.282	8	β_1'
	23.55	2.241	2.237	32	β_1'
	26.00	2.118	2.088	100	α-Cu
	–	–	2.119	55	β_1'
	26.45	2.024	2.024	100	β_1'
	26.75	1.989	1.945	90	β_1'
	29.20	1.835	1.808	46	α-Cu
	31.45	1.716	1.756	3	β_1'
	43.55	1.299	1.278	20	α-Cu
	49.40	1.189	1.170	27	β_1'
89.9	22.57	2.332	2.338	100	α-Al
	26.32	2.019	2.024	47	
	38.88	1.425	1.431	22	
	47.40	1.216	1.221	24	
	50.35	1.163	1.169	7	

d_{exp}: measured value.
d_t: value taken from ASTM sheets and [9].

than 20% aluminium. In alloys with 80–90% Al, the occurrence of a solid solution of copper in aluminium was ascertained (α-Al phase). The interplanar distances of this phase are considerably smaller than those in pure aluminium (Table 2).

In the Cu–Al alloys containing from 0.8 to 6.2% Al, there was a solid solution of aluminium in copper (α-phase). The interplanar distances of this phase increase with increase in aluminium content in the alloy (Table 2). In alloys with Al contents of 6.5%, 8.1% and 11.2% an α-phase and also a metastable martensitic phase β_1' were found to occur. Identification of the β_1' phase was made using the diffraction pattern given by Warlimont and Wilkens [9].

The presence of tetragonal martensite β_1' in electrolytic Cu–Al alloy coatings represents a significant difference from the equilibrium phase composition of metallurgical alloys in which the martensitic structure is achieved due to hardening.

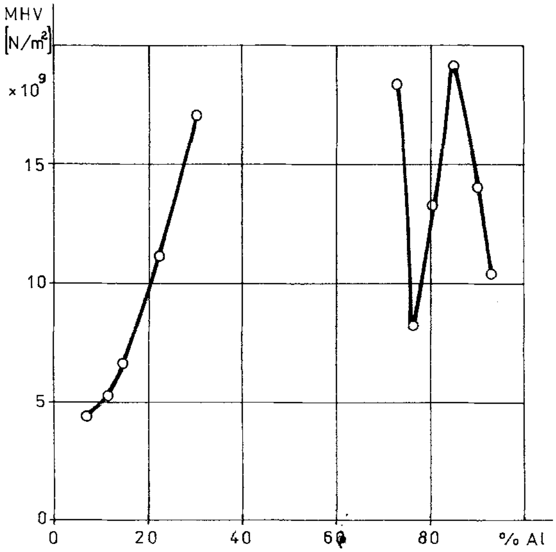

Fig. 5. Microhardness (MHV) of the Cu–Al alloy coatings obtained from the bath, plotted against percentage content of aluminium in the alloy.

The microhardness of the Cu–Al alloy coatings depends on the chemical composition of the alloy (Fig. 5). For low aluminium content (up to 30%) the microhardness of the Cu–Al coatings increases systematically from a value of 1.52×10^9 N m^{-2} for pure copper to a value of 17.2×10^9 N m^{-2} for a Cu–30%Al alloy. This increase may be associated with the formation of a saturated solid solution of aluminium in copper and also with hardening of the alloy due to the formation of β_1' phase. In Cu–Al alloys containing more than 75% Al, the microhardness varies irregularly in the interval from 10×10^9 N m^{-2} to 20×10^9 N m^{-2}. Alloy coatings with an Al content from 30% to 75% exhibit unfavourable properties making it impossible to obtain reliable measurements of their microhardness. Observations of the surface of Cu–Al alloy coatings made with a metallographic microscope immediately after deposition showed that surface morphology is almost independent of the chemical composition of the alloy (Fig. 6).

A characteristic feature of these deposited alloys is the considerable degree of fine crystalline structure, which may be evidence of high polarization in the process of cathode co-deposition of

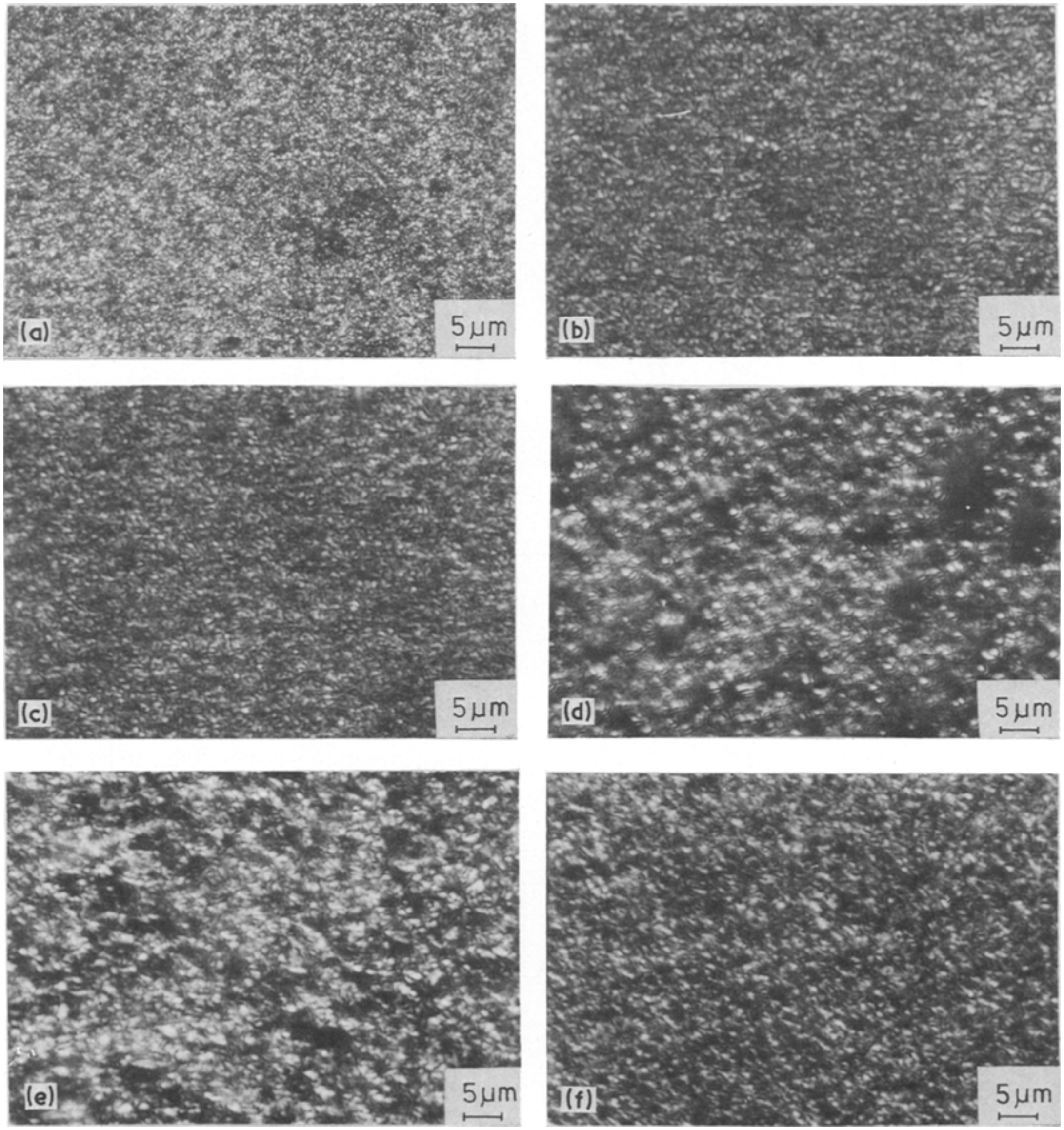

Fig. 6. Surface of Cu–Al alloy coatings observed immediately after deposition in the bath, using a metallographic microscope: (a) Cu–2.9%Al, (b) Cu–6.5%Al, (c) Cu–10.6%Al, (d) Cu–30.6%Al, (e) Cu–74.4%Al, (f) Cu–83.7%Al.

copper and aluminium. With increasing concentration of aluminium in the Cu–Al alloy their colour changes. Alloy coatings containing up to 5% Al are reddish brown, up to about 15% Al the colour is yellow and golden and for higher quantities of Al up to about 30% the colour is grey. Coatings containing between 30% and 75% aluminium are black and covered with a loose, powdery bloom. Cu–Al alloys containing more than 75% aluminium form metallic layers, light grey and silvery in colour.

The presence of a martensitic phase in electrolytic Cu–Al alloy obtained from the bath provided an incentive to conduct studies on the occurrence of the shape memory effect in microelements covered with a layer of this alloy. Tests were carried out on copper wires of diameter 2×10^{-5} m coated with a Cu–10.6%Al alloy layer of thickness 2×10^{-5} m. No shape memory effect was found. The reason for this may be the low value of thermoelastic force in the alloy layer, insufficient to overcome the elastic forces of the

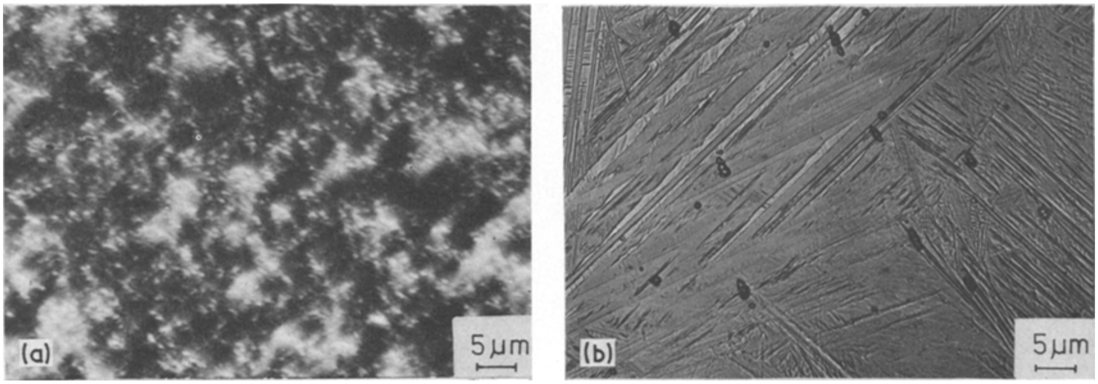

Fig. 7. Polished microsection surfaces observed using a metallographic microscope. (a) Electrolytic Cu–10.6%Al coating obtained from an ethylbenzene/toluene bath; (b) metallurgical Cu–12.4%Al alloy hardened by quenching in water from 1073 K. The specimen has shape memory properties.

copper core. According to [10], the magnitude of the thermoelastic force responsible for the shape memory effect is proportional to the number and size of the alloy grains and the thickness of the martensite lamellae. The electrolytic alloys obtained have a markedly more fine-grained structure than metallurgical alloys exhibiting the shape memory effect (Fig. 7). This fine crystalline structure very probably reduces considerably the magnitude of the thermoelastic force so that it becomes impossible to observe the shape memory effect in electrolytically obtained Cu–Al alloys.

4. Conclusions

By conducting the electrolytic process in a four-electrode system with an ancillary anode copper dissolution circuit and an ethylbenzene bath, it is possible to obtain Cu–Al alloy layers of defined chemical composition. The current efficiency of the cathode alloy deposition process reduces with increasing degree of bath exhaustion. The Cu–Al alloys obtained exhibit a very fine-grained structure. The alloys containing up to about 6% Al and more than 80% Al are single-phase materials: α-Cu and α-Al. In alloys containing from 7 to 12% aluminium, in addition to the solid solution of aluminium in copper, a non-equilibrium martensitic β_1' phase is found. No shape memory effect was detected in microelements coated with Cu–10.3%Al alloy.

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